

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

0 243 653  
A3

(5)

(12)

# EUROPEAN PATENT APPLICATION

(21) Application number: 87104027.5

(31) Int. Cl.<sup>5</sup>: H01M 4/02, H01M 4/62,  
H01M 4/58, H01M 2/14

(22) Date of filing: 19.03.87

A request for correction under Rule 88 of several errors on page 43, 44, 45, 48, 49, 50, 51, 52, 53, 54 and 55 has been filed on 060887.

(30) Priority: 24.03.86 US 843480  
24.03.86 US 842973  
24.03.86 US 843347  
15.08.86 US 896690

(43) Date of publication of application:  
04.11.87 Bulletin 87/45

(84) Designated Contracting States:  
AT BE CH DE ES FR GB IT LI NL SE

(88) Date of deferred publication of the search report:  
23.05.90 Bulletin 90/21

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(54) Cathodic electrode.

(57) A polymer bonded sheet product suitable for use as a cathodic electrode in a non-aqueous battery system wherein the cathodic electrode is a microporous sheet composed of from 2 - 30 weight percent polyethylene, 70 - 98 weight percent of electrically conductive and electrochemically active particulate material and from 0 to 5 weight percent of a plasticizer for the polyethylene. The product of the present invention further includes a cathodic electrode product suitable to be placed in intimate contact with an anodic material comprising a substantially unitary, microporous structure wherein each major surface of said structure is a composition of an inert filler in a polyolefin matrix, the inner core of said structure is a composition of from 70 - 98 weight percent of electrochemically active and electrically conductive particulate material, from 2 - 30 weight percent polyethylene and from 0 to 5 weight percent polyethylene plasticizer and a current collector in contact and extend from the inner core com-

position.

EP 0 243 653 A3



European Patent  
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# EUROPEAN SEARCH REPORT

Application Number

EP 87 10 4027

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	US-A-4 416 915 (D.N. PALMER et al.) * Whole document *	1-5	H 01 M 4/02 H 01 M 4/62 H 01 M 4/58 H 01 M 2/14
A	US-A-4 550 064 (S. YEN et al.) * Column 3, lines 63-68, line 42; column 4, line 20, lines 29-36 *	1-5, 7, 9, 10	
A	US-A-3 351 495 (D.W. LARSEN et al.) * Claim 1; columns 1-6 *	1-9	
A, P	PATENT ABSTRACTS OF JAPAN, vol. 11, No. 240 (E-529)[2687], 6th August 1987; & JP-A-62 52 855 (SHIN KOBE ELECTRIC MACH. CO., LTD) 07-03-1987	1, 6, 8, 9	
A	PATENT ABSTRACTS OF JAPAN, vol. 9, No. 110 (E-314)[1833], 15th May 1985; & JP-A-60 1753 (SHINKOUBE DENKI K.K.) 07-01-1985	1, 6, 8, 9	
A	US-A-4 320 185 (P. BERNSTEIN et al.) * Column 3, lines 33, 39; column 3, line 56 - column 4, line 28 *	1-5	TECHNICAL FIELDS SEARCHED (Int. Cl. 4) H 01 M
A, D	US-A-3 457 113 (M.C. DEIBERT et al.) * Column 4, line 71 - column 5, line 13; column 5, line 60 - column 6, line 19 *	1-5, 9	
A	US-A-3 898 099 (B.S. BAKER et al.) * Column 3, lines 19-30 *	1-5, 9	
A	US-A-4 529 672 (R.A. HOWARD et al.) * Column 2, lines 28-34; claims *	6	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23-02-1989	Examiner CZECH. B.P.
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			



Europäisches Patentamt

European Patent Office

Office européen des brevets

Publication number: 0 243 653

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- (11) Application number: 87104027.5 (51) Int. Cl.<sup>3</sup>: H 01 M 4/02  
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EP 0 243 653 A2

BACKGROUND OF THE INVENTION

The present invention is directed to polymer bonded electrodes useful in a non-aqueous battery and to a battery system containing said electrodes. Further, the present invention is directed to highly filled  $TiS_2$ -polymer bonded electrodes useful in a non-aqueous battery and to a battery system containing said electrodes. Still further, the present invention is directed to a unitary microporous cathodic electrode-separator product having an electrochemically active and electrically conductive inner core and an inert outer portion.

Storage batteries have a configuration composed of at least one pair of electrodes of opposite polarity and, generally, a series of adjacent electrodes of alternating polarity. The current flow between electrodes is maintained by an electrolyte composition capable of carrying ions across electrode pairs. In addition to these active components, there must be an inert material separating the electrodes of opposite polarity. Separators have been used in many forms including grids, blocks, sheets and the like formed from nonconductive materials.

Non-aqueous batteries have certain distinct advantages over other types of storage batteries. They use, as anodes, light weight or alkali metals, such as lithium, lithium-aluminum alloys and the like which are at the far end of the electromotive series. These batteries have the potential for providing much higher gravimetric and volumetric energy densities (capacity per unit weight and volume, respectively) than other types of batteries, due to the low atomic weight of the metal and high potential for forming a battery in conjunction with suitable positive electrodes far removed from the light

weight (alkali) metal electrode (the description herein will use batteries having lithium as the light weight metal anode although other light weight metals can be used) in the electromotive series. The battery can be formed in any conventional physical design, such as cylindrical, rectangular or disc-shaped "button" cells, normally of a closed cell configuration.

The battery components of positive electrode, negative electrode and separator can be in the form of distinct alternating plates in a sandwich design or of a continuous spirally wound design as are well known. The anodic electrodes can be formed, for example, from lithium metal or its alloys on a support, such as a nickel coated screen. The electrolyte can be formed of a non-aqueous solvent or fused or solid electrolyte. Illustrative of known useful non-aqueous solvents include acetonitrile, tetrahydrofuran and its derivatives, propylene carbonate, various sulfones and mixtures of these solvents containing a light metal salt such as lithium salts as, for example, lithium perchlorate, iodide or hexafluoroarsenate and the like. An additional, normally passive component of the battery is a separator membrane located between plates of opposite polarity to prevent contact between such plates while permitting electrolytic conduction. Separators are normally of the form of sheets which possess very low electronic conductivity.

Significant developments have been made in the fabrication of non-aqueous batteries. However, one of the major concerns is the lack of development of a suitable cathode in which the electrochemically cathodic material is present in the form of a porous, flexible, sheet material. The cathodic active material must be bonded into a unitary sheet by a material which is inert with

respect to the other components of the battery as well as being inert and compatible to the active material. The bonding material must be capable of readily forming a uniform sheet. The resultant sheet must have the active material uniformly distributed throughout the length and breadth of the sheet as well as across its thickness to provide maximum effectiveness. The bonding material must be kept to very low amounts of the total sheet material or the cathodic active material will be encompassed by the material and thereby dramatically reduce the conductivity and activity of the resultant cathodic sheet product. Even though present in only small amounts the bonding polymer must be capable of maintaining the sheet integrity and provide resistance to fractures, spalling and disintegration attributable to the expansion and contraction forces encountered in charge-discharge cycling. Polymer bonded electrodes presently known have a number of deficiencies which has limited their utility and, thereby limited the acceptance of an effective non-aqueous battery system. The presently known polymer-bonded electrodes are not capable of being mass produced by a reliable, cost-effective, non-aqueous process. In addition, the majority of known polymer-bonded electrodes exhibit flaking and disintegration when the formed sheet is further processed such as when applied to a current collector and/or during assembly into a battery. A number of bonding polymers have been considered for and used in the fabrication of cathodic polymer bonded electrodes. The most widely used material at the present time is poly(tetrafluoroethylene), commonly referred to as PTFE or by the tradename Teflon. PTFE bonded electrodes

have certain drawbacks which limit their usefulness and ability to provide a highly effective product. For example, the chemical inertness of this polymer causes the fabrication of electrodes to be both difficult and laborious. Generally, it requires initially mixing the active material with an aqueous slurry of PTFE which is then doctored onto a surface and heated to high temperatures (250-400°C) to remove the water and cause bonding. The presence of water and the processing at high temperatures limits the active materials which can be used in forming the electrode product. For example, certain chalcogenides, in particular, titanium disulfide, are known to be unstable in the presence of water. In addition, there is concern that during fabrication residual water will remain and come in contact with the light metal anode such as lithium. Further, PTFE bonded sheets tend to flake and are not free standing unless large amounts of polymer are used. The sheets are conventionally bonded to a current collector screen by pressing them together at high temperatures. This process normally produces a rigid, brittle product which tends to crack and chip. Finally, a major defect of this known class of product is its non-uniformity both in distribution of active material and of porosity. This defect is inherently due to the processing techniques required, especially the evaporation of solvent from the materials causing non-uniformity across its thickness as well as from point-to-point on the sheet product. Patents illustrating formation of polymer bonded electrodes by this technology are U.S. 3,457,113; 3,407,096; and 3,306,779.

Some work has been done to form a product from dry tetrafluoroethylene suspensions to overcome the

incompatibility problems associated with water but such products require sintering at very high temperatures (e.g. 400°C) which also limits the types of active fillers which can be used. Patents illustrating this known technology are U.S. 3,184,339 and 3,536,537.

More recently polymer bonded electrodes have been formed from slurries of EPDM (ethylene-propylene-diene terpolymer) in an organic medium, such as cyclohexane (see "Elastomeric Binders for Electrodes" by S.P.S. Yen et al., J. Electrochem. Soc., Vol. 130, No. 5, Pg. 1107). Other noncrystalline, elastomeric polymers, such as sulfonated ionomers, butyl rubbers and the like have also been used in forming electrodes by a slurry technique (See U.S. 4,322,317). The resultant electrode products formed in this manner exhibit greater elasticity and compatability with the other battery components. However, the defects of non-uniformity of product, poor control of porosity and pore size distribution remain a problem. In addition, electrodes made by this method exhibit severe loss of activity after being subjected to only a few charge/discharge cycles as noted by the low figure of merit reported in U.S. 4,322,317.

It is highly desired to be able to provide a polymer bonded electrode which is capable of being readily fabricated without being labor intensive. Further, it is desired to provide a polymer-bonded electrode which can be formed with a very high content of electrochemically active particulate material, can exhibit a high degree of uniformity, is a flexible material which can be readily formed into desired configuration and can maintain its integrity under the conditions encountered in a battery (including expansion-contraction of cycling). Finally, it is highly desired to provide a polymer-bonded electrode

which is in the form of a sheet of controlled microporosity capable of permitting entry and mobility of electrolyte therein which can thereby increase the electrode's activity. In addition to the above, it is highly desired to be able to provide a polymer bonded electrode especially a  $\text{TiS}_2$ -polymer bonded electrode, which exhibits high charge density; which is capable of sustaining high discharge rates; and which is capable of exhibiting very low capacity loss upon charge-discharge cycling.

Upon initial consideration, it might be assumed that many binding materials could be used as alternatives to the small number of materials presently used and obtain the desired results. However, although there are a large number of polymers available as binders in many applications including as electrode binders, a selection of a specific binder is not obvious to the artisan when attempting to provide a chalcogenide, especially a  $\text{TiS}_2$  filled cathodic electrode because of the many factors which influence the results one obtains with any particular binder. Among the major factors which influences the results obtained are: (1) the solubility of the binder in the organic electrolytes which are required in this application; (2) the chemical stability of the polymer at the electrode potential realizing that many cells are operated at different potentials; (3) the stability of the electrochemically active and electrically conductive materials used in combination with a particular binder and under the conditions needed for fabrication; (4) the ability of the polymer to bind the particulate material into a unitary structure at very low concentrations in order to provide a cathodic electrode with good performance; (5) the ability and ease of

obtaining a uniform distribution of the binder with the active material of the electrode; (6) the ability of the polymer to maintain a stable cathodic electrode capable of undergoing a multiplicity of charge-discharge cycling; (7) the number and ease of the steps required to obtain the desired cathodic electrode; and (8) the safety, the availability of material and the cost. Thus, selection of a polymer for use in forming a high performance electrode containing metal chalcogenides has been a difficult task because of the above factors which impose severe restrictions and limitations.

Applicants disclose herein polymer bonded electrodes including the preferred  $TiS_2$  electrodes which contain ultrafine conductive carbon particulate to enhance the electrical conductivity of the resultant sheet. However, the use of such high surface area conductive carbon reduces the charge density of the electrode and thus reduces the capacity of the battery system. In addition, in some instances the presence of carbon may cause electrolyte decomposition which shortens the life of the battery. Applicants also herein describe sheet products providing a cathode having high electrical conductivity and electrochemical activity without the difficulties associated with the addition of conductive diluents, such as carbon.

Finally, an important component of a battery is the separator. This component is normally in the form of a separate sheet material inserted between electrodes of opposite polarity to prevent their contacting one another. In batteries, such as presently described, the separator must be inert with respect to the other components, be capable of permitting electrolytic conduction through the separator and, in secondary batteries, it must be able to

inhibit and prevent dendritic shorting. Because of the types of polymers used in forming the cathodic electrodes, especially inert Teflon, the separator has been a separate component. This causes additional effort in assembling the cell. Further, its effectiveness is impaired as the separator tends to shrink or migrate thus allowing exposed areas of electrodes. Finally, such individual separator membranes do not provide a means of effectively inhibiting dendrite formation and shorting therefrom. Normally, the edge portions of the electrodes remain exposed to permit dendrite shorting. To overcome this, it has been proposed that the light metal electrode be encapsulated by a separator type envelope. However, this has many complications due to the high reactivity of the light metal, especially lithium.

It is highly desired to form a sheet product suitable for use in forming a cathodic electrode product composed of a polymer-bonded cathodic electrode which is integrally bonded to and encompassed by a composition capable of functioning as an inert microporous separator membrane. It is further highly desired that the sheet product and the cathodic electrode product have good mechanical integrity, be flexible and capable of being formed into various configurations required for different battery designs. It is still further highly desired that cathodic electrode product permit high utilization of the active material and maintain the high activity after subjection to a multiplicity of charge/discharge cycles.

It has now been discovered that a cathodic polymer bonded electrode suitable for use in non-aqueous batteries can be readily formed in a manner which provides a superior electrode and overcomes the processing problems.

associated with Teflon and other presently used polymers as described above.

Summary of the Invention

The present invention is directed to a polymer bonded electrode and to a non-aqueous battery system containing said electrode product in which the electrode is a thin, microporous sheet composed of from 2 - 30 weight percent polyethylene, 70 - 98 weight percent of particulate material composed of electrochemically active and electrically conductive materials and from 0 - 5 weight percent of an organic plasticizer for the polyethylene. The sheet is prepared by forming a substantially uniform mixture of the components with from 20 to 60 volume percent excess of plasticizer, shaping the mixture into a sheet and extracting substantially all of the plasticizer therefrom. The resultant product is a flexible sheet material which possesses a high degree of mechanical integrity, strength and uniformity, has a controlled pore volume of from 15 to 60 volume percent with pore size of narrow distribution and exhibits high conductivity of at least 0.1 reciprocal ohm-cm and preferably at least 0.3 reciprocal ohm-cm.

The preferred product of the present invention is a  $\text{TiS}_2$  polymer bonded electrode of particular components and composition and to a non-aqueous battery system containing said electrode product in which the electrode is a thin, microporous sheet composed of from 6 - 10 weight percent polyethylene of a weight average molecular weight of from 200,000 to 500,000, 90 - 94 weight percent of titanium disulfide and from 0 - 2 weight percent of an organic plasticizer for the polyethylene. The sheet is prepared by initially forming a substantially uniform mixture of

the components with excess plasticizer, shaping the mixture into a sheet, extracting a portion of the plasticizer, compressing the sheet and then extracting the remainder of the plasticizer. The resultant product is a flexible sheet material which possesses a high degree of mechanical integrity, strength and uniformity, has a controlled pore volume of from 15 to 25 percent with pore size of narrow distribution and exhibits high conductivity of at least 0.15 reciprocal ohm-cm and preferably at least 0.3 reciprocal ohm-cm.

The present invention is also directed to a microporous unitary chalcogenide cathodic electrode-separator product formed using the sheet product of the present invention, wherein the electrode product comprises an inner core having a composition which is highly filled with an electrically conductive and electrochemically active particulate material and an outer portion forming each of the two major surfaces of the sheet product composed of a composition of from about 7 - 36 weight percent polyolefin having weight average molecular weight of at least 100,000, from about 50 - 93 weight percent of an inert filler and from 0 - 15 weight percent of a plasticizer for said olefin, and an electronically conductive material in intimate contact and extending from the inner core composition.

The polymer bonded electrode product formed according to the present invention is capable of exhibiting high degree of activity even after subjection to a large number of charge/discharge cycles.

#### Detailed Description of the Invention

The polymer bonded electrode of the present invention is in the form of a thin sheet which is required to be

formed from a homogeneous admixture of polyethylene, a plasticizer for the polyethylene, and particulate material having a combination of electrochemical active and electrically conductive properties as are described herein below.

The polymer electrode of the instant invention is formed through a series of precursor materials. Generally, a uniform admixture is initially formed of polymer, plasticizer and particulate material. The admixture is capable of exhibiting sufficient flow and rheological characteristics to permit the admixture to be readily processed and shaped at relatively low temperatures (i.e. 25°C-170°C). An initial sheet is formed from the admixture. The plasticizer component is then removed from the initial sheet. This removal normally occurs subsequent to the forming of a laminate in which a metal screen (a current collector) is laminated to a sheet or sandwiched between two sheets to provide an electrode product. The final electrode product, having had the plasticizer component substantially removed, is a highly filled (normally 85 wt. % or greater) product useful as a polymer bonded electrode.

The present invention requires the utilization of polyethylene of high density. The polyethylene should have a weight average molecular weight of at least about 150,000 and is preferably selected from higher molecular weights such as from about 200,000 to 5,000,000. The most preferred polyethylenes are homopolymers of high molecular weight such as of a weight average molecular weight of 200,000 to 500,000. The term "polyethylene", as used herein and in the appended claims, shall mean high density polyethylene homopolymers or polyethylene copolymers in which copolymer is formed from olefinic monomers such as

ethylene, propylene, butene-1, acrylate and the like with the major (at least 80 percent) olefinic monomer being ethylene.

The polymer component used in forming the subject electrode product can be comprised of a mixture of a high molecular weight polyethylene and a low molecular weight polyethylene. The mixture can be formed from about 5 - 95 weight percent of a high molecular weight polymer and a corresponding 95 - 5 weight percent of a low molecular weight polymer. The term "high molecular weight polymer" is intended to refer to a polymer having a weight average molecular weight of at least 250,000 and "low molecular polymer" refers to a polymer having a weight average molecular weight of from about 100,000 to 250,000.

The plasticizer of the instant composition must be present in the initial formulating and processing to form an initial sheet product, as more fully described below. The plasticizer provides the means of fabricating the composition to a uniform consistency and to aid in inducing and controlling the degree of porosity, the pore size distribution and uniformity of porosity throughout the resultant sheet product.

Plasticizers suitable for the instant invention are compounds which are capable of plasticizing polyethylene under the elevated temperature and/or pressure process conditions, are substantially inert with respect to the particulate material used herein, and are substantially soluble in an organic solvent which is a non-solvent with respect to the polymer component described above and the particulate material described below which are used in forming a particular composition. Representatives of such plasticizers are organic esters, such as sebacates, phthalates, stearates, adipates and citrates; epoxy

compounds such as epoxidized vegetable oil; phosphate esters such as tricresyl phosphate; hydrocarbon materials such as petroleum oil including lubricating oils and fuel oils, hydrocarbon resin and asphalt and pure compounds such as eicosane; coumarone-indene resins and terpene resins; tall oil and linseed oil. The preferred plasticizers are hydrocarbon materials and most preferred plasticizers are selected from petroleum oils. The plasticizer is generally substantially free of water (anhydrous) and, therefore, compatible with the subject battery system.

The organic plasticizer used herein aids in fabricating the sheet product and in imparting microporosity to the resultant sheet. The void volume of the resultant sheet will be directly dependent upon the amount of plasticizer used to form the initial composition and the amount of plasticizer extracted to provide the final sheet product. Void volumes of the final sheet product may range from about 15 volume percent to about 60 volume percent with from about 25 to 40 volume percent being preferred. Higher ranges are normally acceptable for sheet products having higher cross-sectional dimensions. The sheets void volume is of a microporous character which generally have narrow distribution and are of low mean diameter (i.e. 0.05 to 0.5 microns) and can be determined by standard mercury intrusion techniques.

The particulate material required in forming the present admixture and the resultant sheet is composed of the cathodic electrochemically active and electrically conductive materials. They must be in particulate form. Smaller particle size material (such as a mean particle size of about 25 microns or less and preferably less than 10 microns) is preferred to enhance intimate contact.

between the particles of electrochemically active material contained in the resultant electrode. The term "electrochemically active" refers herein and in the appended claims to the ability of a material to enter and participate in a redox reaction during the operation and in the environment of an electrochemical cell. The term "electrically conductive" refers herein and in the appended claims to the ability of a material to exhibit low resistance to the passage of electrons.

The particulate material used herein will be selected from the chalcogenide compounds described below alone or with electrically conductive diluent also described below. The materials should be such as to provide an electrode sheet product capable of exhibiting an overall conductivity of at least about 0.1 reciprocal ohm-cm. When a cathodically-active material has low electrical conductivity (the majority of the chalcogenide exhibit less than about 0.001 reciprocal ohm-cm) they must be used in combination with conductive diluent, as described below.

The particulate material can be one or more of the chalcogenide compounds which have the appropriate crystal structure to exhibit electrical conductivity. The compounds are selected from sulfides, oxides, selenides, and tellurides of titanium, zirconium, hafnium, niobium, manganese, copper, iron, tantalum, chromium, and vanadium. In general, such chalcogenides contain about 1.8 to about 3.2 atoms of the chalcogen per metal atom. Advantageously, when forming a secondary battery the cathodic electrode is preferably selected from a chalcogenide of titanium and most preferably electrochemically active and electrically conductive titanium disulfide. When forming a primary battery the

preferred chalcogenides are formed from vanadium, such as  $V_2O_5$ , iron and copper especially the sulfides of iron and copper. Also, among the chalcogenides, those which contain about 1.8 to about 2.1 atoms of chalcogen per metal atom, commonly referred to as the dichalcogenides, are preferred.

Examples of cathode-active materials which may be useful and which are selected from the above-mentioned chalcogenides are titanium disulfide, zirconium disulfide, hafnium disulfide, niobium triselenide, tantalum disulfide, vanadium disulfide, vanadium diselenide and vanadium ditelluride as well as vanadium oxide such as  $V_3O_8$  and  $V_5O_{13}$ . Also included are the chalcogenides having more than one of the mentioned metals, e.g.,  $V_{0.25}Ti_{0.75}S_{2.0}$ . Also included are those chalcogenides having metals other than those described above included, e.g., vanadium iron disulfide. Lastly, it should be noted that while the trichalcogenides and dichalcogenides are described, the present invention is not limited thereto and may include, for example, the pentachalcogenides and the like.

It has been unexpectedly found that by using particulate material of the particle size herein described one obtains an electrode of high energy density and stability. The mean particle size of the material should be 30 microns or less preferably 20 microns or less and most preferably 15 microns or less. Smaller particle size material is preferred to enhance intimate contact between the particles.

In a preferred embodiment, the polymer-electrodes of the present invention are formed with the particulate material, titanium disulfide. In addition to the titanium disulfide, the particulate material can also contain minor

amounts of (less than about 20 weight percent) cathodic-active particulate material selected from sulfides, selenides and tellurides of vanadium, hafnium, niobium, zirconium or tantalum as well as selenides and tellurides of titanium and oxides of vanadium, or chromium and mixtures thereof. The preferred resultant polymer bonded electrode has titanium disulfide as the sole cathodic electrochemical active material. Examples of cathode-active materials which may be used in combination with titanium disulfide, are zirconium disulfide, hafnium disulfide, niobium triselenide, tantalum disulfide, vanadium disulfide, vanadium diselenide and vanadium ditelluride. Also included are materials having more than one of the mentioned metals, e.g.,  $V_{0.25}Ti_{0.75}S_{2.0}$ . Also included are those materials having additional metals other than those described above included e.g. vanadium iron disulfide, sodium titanium disulfide and lithium titanium disulfide.

The particulate chalcogenide may further comprise minor amounts (up to about 30 weight percent preferably up to about 20 weight percent) of conductive diluent such as high surface area conductive carbon black. The diluent is normally of ultrafine particle size of from about 1 to 100 millimicrons and have a (BET) surface area of at least  $40 \text{ m}^2/\text{g}$ , preferably at least  $70 \text{ m}^2/\text{g}$  and most preferably from  $70$  to  $2000 \text{ m}^2/\text{g}$ . The carbon can serve several roles to enhance the subject electrode. In instances where the particulate chalcogenide used has good electronic conductivity, the carbon merely acts as an electrical conductive bridge between particles of chalcogenide to further enhance the total properties of the resultant electrode. Where the chalcogenide has poor electronic conductivity i.e.  $V_2O_5$  (high resistance) the conductive

diluent provides a means for carrying the electron to the current collector from the electrochemically active chalcogenide site.

The particulate material, either singly or in combinations as described herein, must be capable, when placed in the present polymer matrix, of causing the resultant electrode sheet product of this invention to exhibit an overall electrical conductivity of at least about 0.1 (preferably 0.3) reciprocal ohm-cm. It is known that most materials which are capable of exhibiting cathodic activity have normally been found to provide very low conductivity of, for example, less than 0.001 reciprocal ohm-cm. in prior art products.

In addition to the above described components, the initially formed admixture may further contain conventional stabilizers, antioxidants, wetting agents, processing aids or mixtures thereof. Representative of stabilizers are 4,4-thiobis(6-tertbutyl-m-cresol) sold commercially under the tradename "Santox" and 2,6-ditert-butyl-4-methylphenol sold commercially under the tradename "Ionol". Examples of known commercially available wetting agents include sodium alkyl benzene sulfonate, sodium lauryl sulfate, dioctyl sodium sulfosuccinate, and isooctyl phenyl polyethoxy ethanal. Processing aids include stearates, graphite and the like.

The above-described components can be readily formed into a substantially homogeneous admixture. The initial admixture should be formed by blending from about 5 to 35 (preferably 5 - 20) volume percent polymer, from about 25 to 75 (preferably 40 to 60) volume percent of particulate material and from about 20 to 50 volume percent of polymeric plasticizer.

The blending of the components can be readily accomplished by conventional means such as by initially mixing at room temperature in a blender and then in a Banbury, Brabender or sigma blade mixer or the like at moderate (about 25 to about 170°C, preferably from about 120 to about 160°C) temperatures. The blending and processing is preferably done under dry conditions to avoid water pick-up by the materials.

It has been found that even though the present product has extremely high particulate content, the admixtures required by the present invention exhibit rheological properties which permit them to be readily shaped and formed into thin sheet products of less than about 50 mils, preferably less than about 20 mils. It must be understood that the particular thickness can be customized by the artisan based on the battery design and its acceptable drain rate. Sheet products and electrodes therefrom can be made of less than 5 mils and even less than 3 mils thickness. Sheet products made by presently known conventional techniques can not be formed of such thin dimensions and maintain good mechanical properties as is attainable by sheet products of the present invention. The term "sheet" as used herein and in the appended claims refers to a shaped product having extensive length and breadth dimensions and of thin cross-section and which may have major surfaces which are substantially flat or of a predetermined design. The initial sheet product can be readily formed from the admixture by subjecting the admixture to extrusion, calendering, injection molding or compression molding processing. All of these processing means are capable of producing the initial sheet in large volume using low labor involvement. The most preferred method is extrusion of the admixture using a conventional

extrusion apparatus to continuously provide initial sheet product.

The forming of the initial sheet (a sheet having high levels of plasticizer therein) can be readily accomplished at moderate operating conditions, including low temperatures of from about 25 to 175°C and preferably from about 120 to 160°C. Such temperatures allow formation of sheet product using components normally deemed unsuitable under known slurry processes. Further the present process provides a sheet which is freestanding and has substantial uniform distribution of particulate material throughout its length and breadth dimensions as well as across its cross-sectional dimension.

The initially formed sheet can be readily made into a suitable cathodic electrode by laminating a conventional current collector with at least one sheet of the present invention. The plasticizer component can be extracted, as described below, prior or subsequent to lamination with the current collector. It is preferred to initially form the laminate structure of at least one sheet with a suitable current collector and then extract the plasticizer material.

The current collector is normally a screen, grid, expanded metal, woven or non-woven fabric or the like formed from efficient electron conductive materials such as carbon, or metals such as copper, aluminum, nickel, steel, lead, iron or the like. The current collector, when laminated to the final sheet product (a sheet substantially comprising particulate material bonded by very low amounts of polyethylene) of the present invention, provides a low electronic resistance path between the active material and the battery terminal.

The sheet product, with or without the presence of

plasticizer, is a pliable and moldable material which can be readily laminated to the collector screen by concurrently passing a screen and at least one sheet through a set of nip rollers or the like to press (under low pressure and preferably at moderate temperatures of about 25 to 170°C) to produce a laminate product. It is preferred that the laminate be of a configuration of a screen sandwiched between (and thereby embedded in) two sheets although a laminate of a single sheet and single screen may be desired in certain applications. The laminate can be most readily formed by utilizing an initial sheet product immediately after its production to utilize the sheet in its elevated temperature state.

The plasticizer contained in the initial formed sheet should be substantially completely removed by means of extraction using suitable solvent. The composition of the resultant electrode will depend upon the degree of extraction of the plasticizer. The plasticizer can be substantially completely removed, leaving a microporous polymeric sheet product which is highly filled with cathodic active material. The resultant sheet product exhibits good physical properties and a high degree of microporosity. The exact degree of microporosity is induced and regulated to a large degree by the amount of plasticizer used and extracted. The microporosity character of the resultant polymer bonded electrode provides a means to permit the electrolyte to be in intimate contact with a very high percentage of the particulate material. It is believed, although not meant to be a limitation on the present invention, that the microporous structure of the sheet permits the particles residing in the interior of the sheet to be more active.

The procedure for extraction of the plasticizer from a sheet product is well known and is not meant to form a part of the present invention, per se. A single stage extraction can be used. The solvent or extraction conditions should be chosen so that the polyolefin and particulate material are essentially insoluble. For example, when petroleum oil is to be extracted from the formed sheet, the following solvents are suitable; chlorinated hydrocarbons, such as trichloroethylene, tetrachloroethylene, carbon tetrachloride, methylene chloride, tetrachloroethane, etc., as well as hydrocarbon solvents such as hexane, benzene, petroleum ether, toluene, cyclohexane, gasoline, etc. Aqueous solvents should not be used.

The extraction temperature can range anywhere from room temperature up to the melting point of the polyolefin as long as the polyolefin does not dissolve. The temperature can be maintained such that all components remain stable and are not adversely effected.

The time of the extraction will vary depending upon the temperature used and the nature of the plasticizer or filler being extracted. For example, when a higher temperature is used, the extraction time for an oil of low viscosity can be a very short time of up to only a few minutes, whereas if the extraction is performed at room temperature, the time requirement will be greater.

The final composition of the polymer-bonded electrode sheet product will depend upon the original composition and the degree of extraction of the plasticizer from the sheet product. The extracted sheet normally has from about 2 to 30 weight percent polyethylene, about 70 to 98 weight percent particulate material, and from about 0 to 5 weight percent plasticizer. The more preferred electrode

comprise a mixture of from 4 to 15 weight percent polyolefin, 85 to 96 weight percent particulate material, and from 0 to 3 weight percent plasticizer.

In a preferred embodiment, 8 weight percent polyethylene, 71 weight percent particulate material, and 21 weight percent plasticizer are blended together, extruded to provide a flat sheet and then sufficient plasticizer is extracted to provide a finished electrode sheet composed of 10 weight percent polyolefin, 89 weight percent particulate material, and 1 weight percent plasticizer.

#### Preferred Embodiment I

A preferred polymer bonded sheet product suitable for use as a cathodic electrode in non-aqueous batteries is a microporous sheet composed of a specific combination of components and amounts of from 6 - 10 weight percent polyethylene having a molecular weight of 200,000 to 500,000, 90 - 94 weight percent of titanium disulfide particulate material and from 0 to 2 weight percent of a plasticizer for the polyethylene; the sheet having a void volume of from 15 to 25 percent. The microporous sheet is not required to contain conductive diluent such as carbon to achieve the highly effective product.

The formed electrode exhibits high charge density, is capable of sustaining high discharge rates and is capable of exhibiting very low capacity loss upon charge-discharge cycling.

The preferred embodiment requires the utilization of polyethylene of high density which has a weight average molecular weight of 200,000 to 500,000. Polyethylene homopolymers are most preferred.

Suitable organic plasticizers used herein are the same as described herein above. They are used herein to aid in fabricating the sheet product and in imparting microporosity to the resultant sheet. The void volume of the resultant sheet will be directly dependent upon the amount of plasticizer contained in the intermediate sheet prior to subjecting the sheet to compression and to the amount of plasticizer extracted therefrom to provide the final sheet product. Void volumes of the final sheet product may range from 15 to 25 volume percent with from about 15 to 22 volume percent being preferred. Electrodes with higher ranges of void volume have been found to exhibit much higher capacity loss. The sheets void volume is of a microporous character which generally have narrow pore size distribution and are of low mean diameter (i.e. 0.01 to 0.5 microns) and can be determined by standard mercury intrusion techniques.

The particulate material required in forming the present admixture and the resultant sheet is composed of the cathodic electrochemically active and electrically conductive titanium disulfide. The titanium disulfide must be in particulate form. The mean particle size of the material should be 30 microns or less and preferably 15 microns or less. Smaller particle size material is preferred to enhance intimate contact between the particles of electrochemically active material contained in the resultant electrode. It has been unexpectedly found that by using titanium disulfide and polyethylene in the amounts and of the type described hereinabove in an electrode having the particular void volume of from 15 to 25 volume percent one obtains an electrode which can sustain its capacity over a large number of charge-discharge cycling.

In addition to the above described components, the initially formed admixture may further contain conventional stabilizers, antioxidants, wetting agents, processing aids or mixtures thereof as described herein above.

The above-described components can be readily formed into a substantially homogeneous admixture. The initial admixture should be formed by blending from about 3 to 30 (preferably 12 to 20) volume percent polymer, from about 27 to 76 (preferably 40 to 55) volume percent of  $\text{TiS}_2$  and from about 20 to 70 volume percent of polymeric plasticizer. The blending of the components can be readily accomplished by conventional means as described herein above.

The initially formed sheet can be formed into a final sheet product suitable for use as a cathode through the formation and processing of an intermediate sheet product. The formed initial sheet, as described hereinabove contains a very high percentage of plasticizer. Removal of substantially all of the plasticizer would provide a sheet product highly loaded with  $\text{TiS}_2$  and having a large void volume. Such sheet products do not exhibit the ability to sustain its capacity over a large number of charge-discharge cycling. However, when the final sheet is formed as described herein below, one unexpectedly achieves the desired product. Such a final sheet can be achieved by processing an initially formed sheet into an intermediate sheet having from about 10 to 22 volume percent plasticizer therein. Such an intermediate sheet can be formed by a variety of manners such as by (a) removing a portion of the plasticizer contained in the initial sheet to reduce the plasticizer content to between 10 and 22 volume percent; (b) removing substantially all

Neu eingereicht  
Nouvelles 26.11.1963

of the plasticizer contained in the initial sheet and then causing a fixed amount of plasticizer to be absorbed into the sheet to provide an intermediate sheet having plasticizer content of from 10 to 22 volume percent; or (c) forming the initial sheet from mixtures of a first and a second plasticizer which have mutually exclusive solubility in two solvents useful for extraction, removing the first plasticizer such as by extraction or the like with a solvent which is a substantial non-solvent for the second plasticizer therein to thus provide an intermediate sheet having from 10 to 22 volume percent of the second plasticizer. The intermediate sheet is then compressed such as by passing the sheet through nip rollers or the like to cause the sheet to be substantially nonporous. The compressed intermediate sheet is then subjected to extraction or the like to remove substantially all of the plasticizer contained in the intermediate sheet to provide a resultant sheet product having 6 to 10 weight percent polyethylene, 90 to 94 weight percent  $\text{TiS}_2$  and from 0 to 2 weight percent plasticizer as described hereinabove.

The formed sheet, either as the initial, intermediate or final sheet, can be readily made into a suitable cathodic electrode by laminating a conventional current collector with at least one sheet of the present invention. The plasticizer component can be extracted, in the same manner as described above either prior or subsequent to lamination with the current collector. It is preferred to form the laminate structure of at least one sheet with a suitable current collector prior to extraction of all of the plasticizer material. One preferred mode is to form the laminate structure during the compression of the intermediate sheet, as discussed above.

The sheet product, with or without the presence of plasticizer, is a pliable self supporting and moldable material which can be readily laminated to the collector screen in the manner described above. The final product, having had the plasticizer component substantially completely removed, is composed of from 6 to 10 weight percent of polyethylene and of from 90 to 94 weight percent  $TiS_2$ . The resultant product has a void volume of from 15 - 25 percent and is useful as a polymer bonded electrode.

#### Preferred Embodiment II

Another preferred embodiment of the subject invention is directed to a unitary microporous chalcogenide (preferably  $TiS_2$ ) cathodic electrode-separator product. It shall be seen that the resultant product shall have an inner core having an electrochemically active and electrocally conductive composition substantially as described for the sheet products above and, in addition, shall have outer surfaces which are inert with respect to the battery system but which permits electrolytic passages and prevents dendristatic formation.

For clarity, the electrode-separator product of the present invention shall be described herein using certain terms which shall have the following definitions:

"sheet" or "membrane" shall mean a broad substantially planer material having major surfaces and edges defining its length, breadth and thickness. The sheet may be inert or passive with respect to an electrochemical reaction or may be formed with electrochemically active and electrically conductive material(s).

NCV-28-

"First sheet" or "core material" shall, refer to a composition containing a high percentage of cathodic electrochemically active and electrically conductive particulate material or mixture of materials.

"Second sheet" or "outer surface material" shall refer to a composition which is substantially inert and passive with respect to the electrochemical reaction of a light metal containing battery cell.

"Sheet product" shall with respect to the electrode-separator product, refer to a unitary sheet material formed from at least one first sheet and at least one second sheet.

"Electrochemically active" shall refer to material which is capable of undergoing redox reaction with an alkali metal, especially Li, (a Group 1A metal of the Periodic Chart of Elements) under the conditions encountered by a battery cell in which the material is contained.

"Electrically conductive" or "electronically conductive" shall refer to material which is capable of exhibiting electronic conductivity of at least  $10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$ .

"Current collector" shall mean a screen, foil, grid, web, woven or non-woven fabric or the like formed from an efficient electronically conductive material such as carbon or a conductive metal.

"Electrode product" shall with respect to the electrode-separator product, refer to mean a unitary, microporous sheet having a core formed from a composition of at least one first sheet, at least one current collector in intimate contact with the composition of the first sheet and each major surface of the unitary microporous sheet composed of a composition of a second

sheet which is in intimate contact and bonded to the first sheet composition.

The first sheet or core of the subject cathodic electrode is generally formed by initially blending a uniform admixture of polyethylene, plasticizer for the polyethylene and particulate material composed of chalcogenide material alone or with other particulate material, as described hereinabove. The specific descriptions given above for the chalcogenide sheet product and for the  $TiS_2$  sheet product (preferred embodiment I) are applicable in describing the components of the first sheet herein.

The components used to form the first sheet can be readily formed into a substantially homogeneous admixture by initially blending from about 5 to 35 (preferably 5 - 20) volume percent polymer, from about 25 to 75

(preferably 40 - 60) volume percent of particulate material and from about 20 to 50 volume percent of polymeric plasticizer. The amounts of each component can be adjusted by the formulator to provide sufficient plasticizer to enhance processability and provide for desired microporosity while limiting the polymer-particulate ratio to provide a resultant sheet having very low ratio of polymer to particulate material.

The first sheet after removal of plasticizer, as described below, should have a composition of from 2 - 30 (preferably 4 - 15) weight percent polyethylene; from 70 - 98 (preferably 85 - 96) weight percent electrochemically active and electrically conductive particulate material; and from 0 - 5 (preferably from 0 to 2) weight percent of plasticizer for the polyethylene.

A second sheet or outer surface material of the subject electrode is formed from an initial blend of a

polyolefin, an inert filler and a plasticizer for the polyolefin. The polyolefin is preferably high density polyethylene or a polypropylene. The most preferred material is a polyethylene which is the same as or similar to that used in forming the first sheet of the same resultant sheet product. The polyolefin should have a weight average molecular weight of at least 100,000, preferably from 150,000 to 2,000,000 and most preferably from 150,000 to 500,000. The polyolefin can be a homopolymer or copolymer formed from a mixture of hydrocarbon olefinic monomers or with other olefinic monomers such as acrylic acid or esters. Representative of polyolefins which may be used are polyethylene, polypropylene, polybutene, ethylene-propylene copolymer, ethylene-butene copolymer, ethylene-acrylic acid copolymer and the like. Further, the polyolefin can be a mixture of two or more polyolefins of similar or different weight average molecular weight. For example the mixture can be composed of a high (greater than 500,000) and a low (100,000 - 500,000) molecular weight polymers.

The plasticizer for the polyolefin of the second sheet must be an organic material which is substantially free of water (anhydrous). Examples given above with respect to the first sheet are applicable here. It is preferred that the second and first plasticizers have similar solubility characteristics. That is that they are soluble in a common organic solvent which is a non-solvent and inert with respect to the other components of the resultant sheet product.

The second sheet product should contain a filler which is inert and passive with respect to the other components of the resultant sheet product and passive with respect to the electrochemical reaction of a non-aqueous

battery cell, such as a lithium battery. Examples of suitable inert and passive filler material include metal oxides such as those of silicon, aluminum, calcium, magnesium, barium, iron, zinc and tin; minerals such as mica, attapulgite, kaolite, talc, deatomaceous earth and the like; precipitated metal silicates, such as calcium silicate and aluminum polysilicate; glass particles and the like. The most preferred materials are selected from titania, alumina and silica. It is preferred that the inert materials should have a particle size of from about 0.01 to about 10 microns in diameter and have a surface area of from about 100 to 4000 m<sup>2</sup>/cc with from about 100 to 500 m<sup>2</sup>/cc being preferred.

The components of the second sheet are present in the initial admixture in from about 5 to 35 (preferably 10 - 20) volume percent polyolefin, from about 25 to 70 (preferably 30 - 60) volume percent of inert filler, and from about 20 to 60 (preferably 30 - 50) volume percent of plasticizer. The resultant sheet after removal of plasticizer is a substantially homogeneous composition of from 7 - 35 weight percent polyolefin, from 50 - 93 weight percent filler and from 0 - 15 weight percent plasticizer.

The initially formed admixture for forming each first and second sheet may further contain conventional stabilizers, antioxidants, wetting agents, processing aids or mixtures thereof as described for the chalcogenide sheet products herein above.

Each of the first and second sheets can be formed in substantially the same manner as has been described as applicable to form the chalcogenide sheet product. Each admixture can be initially shaped and formed into thin sheets of less than about 50 mils and preferably less than about 20 mils. The total thickness of the resultant

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Nouvellement déposé

electrode product should not exceed about 60 mils. In a preferred embodiment, a first sheet and a second sheet can be concurrently formed by coextrusion and placed in intimate contact through the use of nip rollers or the like to form a unitary sheet product composed of one first sheet and one second sheet. It is preferred that the first sheet and second sheet be combined into a unitary sheet product prior to extraction of the plasticizer(s) used. The formation can be readily accomplished at moderate operating conditions, including low temperatures of from about 25 to 175°C. These conditions permit utilization of components normally deemed unsuitable in forming cathodic electrodes by presently known methods.

The sheet product described hereinabove can be used in forming a unique cathodic electrode product suitable for use in a non-aqueous battery system. The sheet product must be placed in contact with a conventional current collector in a manner to cause the first sheet component of the sheet product to be in intimate contact with the current collector. Contacting of the collector with the sheet product is normally done by pressing or passing the materials through nip rollers or the like to cause the collector to be sufficiently embedded in the first sheet component to remain in intimate contact thereafter. It is preferred to embed the current collector in the first sheet prior to further contact with a second sheet components.

The current collector can be positioned to be in contact with a first sheet of a sheet product described above for use as the single cathodic electrode of a cell or can be positioned between two first sheets or two sheet products so that the first sheet of each sheet product is in face to face and in intimate contact with the

collector. In both cases the resultant sandwiched product will thus have a second sheet on each exposed major surface. Alternately, a single sheet product and a single second sheet can have a current collector placed between them (again with the collector being adjacent to the first sheet of the sheet product) and pressed together to form a sandwiched product.

The plasticizer component of each sheet can be extracted, as described below, from each individual sheet, from each sheet product or subsequent to the lamination of the sheet product with a current collector and where appropriate with another sheet product or second sheet. It is most preferred that the extraction be conducted after lamination has been completed.

Although one or more of the sheets used in forming the present sheet product and electrode product can be subjected to extraction processing prior to being united with other sheets to form the final (sheet or electrode) product, it is preferred to conduct extraction subsequent to forming the final product, most preferably subsequent to forming the electrode product. It is believed, although not meant to be a limitation on the claimed invention, that the presence of plasticizer provides a further aid in having the resultant electrode product be a substantially fused and unitary structure. The plasticizer provides a conduit which permits the polymers of each sheet to migrate at the sheets interface to provide a resultant product of an integral, unitary polymer matrix.

The procedure for extraction of the plasticizer component from each sheet is well known and is not meant to form a part of the present invention, per se. The procedure shall be discussed herein with respect to

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extraction of plasticizer from an electrode product which is the preferred embodiment. The solvent(s) and extraction conditions should be chosen so that the polyolefin and filler of each second sheet and the polyethylene and electrically conductive and electrochemically active particulate material of each first sheet are essentially insoluble. Where the plasticizer used to form each sheet is the same material or has substantially the same solubility characteristics, one can use a single stage extraction. However, if plasticizer components of different solubility characteristics are used (either as part of forming a single sheet or for different sheets) a multiple stage extraction may be required. Numerous solvents as described above can be used to cause removal of the plasticizer with the particular solvent(s) depending upon the particular plasticizer material to be removed.

The electrode products are substantially unitary structures which is believed due to the nature of the materials used, the requirement to have a plasticizer present in at least some of the sheets used to form the electrode product and the forces the components undergo during formation of the product. The electrode product has substantially no distinct interface boundary between the sheet components used in its formation and can be viewed as a gradient change across the electrode product's thickness or cross-section with the outer portion being an inert (with respect to the cathodic and anodic electrochemically active materials, the electrolyte and its carrier) portion and the inner body being cathodic active. The electrode product has microspores throughout its body. The nature of the porosity (average pore size diameter and/or pore volume) may vary from outer

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Nouvellement déposé

to inner portion and is preferably of a larger mean diameter and/or pore volume in the outer, inert portion and of smaller values in the inner, cathodic segment.

Void volumes of the final sheet product may range from about 15 volume percent to about 60 volume percent with from about 25 to 45 volume percent being preferred. The sheets void volume is of a microporous character which generally have narrow distribution and are of low mean diameter (i.e. 0.05 to 0.5 microns) and can be determined by standard mercury intrusion techniques.

The ability to form the unitary structure may be (the theories discussed herein with respect to the structure of the subject electrode product are not meant to be a

limitation on the present invention but only a means of describing the present invention so as to be fully understood by those skilled in this art) due to the nature of the polymer used in each sheet component. The close chemical nature of the polymers and their compatibility permits them to readily migrate from one sheet into an adjacent sheet. The plasticizer component(s) also aid in providing a unitary structure. The presence of a plasticizer, especially where it is common to all sheets or at least where there is common solvency, causes the polymer to migrate and intermesh the sheets when they are in contact. Additionally, the movement of the plasticizer as it is being removed from the product further forces the polymers to flow to further enhance the unitary nature of the resultant product.

A sheet product of the present invention can be readily formed from a first sheet and a second sheet wherein each sheet has certain predetermined length and breadth dimensions whereby at least one dimension and preferably both dimensions of the first sheet are less

NOUVEAU  
-36-

than those of the second sheet so that when the first and second sheets are placed against one another and caused to fuse together it provides a sheet product in which the second sheet extends beyond the dimension of the first sheet with the first sheet substantially centered therebetween. When this initially formed sheet product is used to form an electrode product, it can be used with either a second sheet or another sheet product having a second sheet which has substantially the same dimensions as the second sheet of the initially formed sheet product. The electrode product thus formed will have the first sheet(s) substantially completely encapsulated within second sheets which form the outer major surfaces of the electrode product. Alternately, a second sheet can be wrapped around a first sheet to envelope the first sheet therein. This can be readily done with the present material as they exhibit a high degree of flexibility and mechanical strength. The current collector will be in contact with the first sheet and extend beyond at least one edge of the electrode product as a contact means.

The resultant electrode product of the present invention is a substantially unitary product having flexibility and good tensile properties. It is capable of being readily formed under substantially anhydrous condition which, in turn, provides it with high stability when used in conjunction with a light metal, such as lithium. The resultant electrode product can be placed adjacent to anodic electrodes without the need of a separate insulating element and inhibits dendrite formation between cathodic and anodic elements of the battery. In addition it has been observed that the present electrode product is capable of undergoing a large

-37-

amount of charge/discharge cycles to aid in providing an effective battery system.

Test Procedures

The porosity volume percents or void volume percent were calculated for the resultant sheet product by calculating the wet weight minus dry weight divided by the sheet product's geometric wet volume.

Charge/Discharge cycling was performed on cells having the subject sheet using a Princeton Applied Research Model 363 galvanostat. The galvanostat was powered and monitored with an Analog Devices MAC 5000 microcomputer which controlled the current passing through the cell and measured the current passing through the cell and measured the current voltage and charge throughout the cycle.

The electrical conductivity of the resultant sheet products were measured with a Yellow Spring Instrument Conductivity Bridge at 1 KHz by placing a nickel metal clamp on each of the two opposite ends of the specimen to be tested in such a manner as to have a free sample spacing of 1 cm by 1 cm not covered by the clamps. The thickness of the samples were measured. The clamps were connected to a conventional conductivity bridge and the resistance of the samples were measured. To check the accuracy of the measurements, the clamps were adjusted to a spacing of 2 cm by 1 cm and the resistance remeasured.

The porosity volume percents or void volume percent were calculated for the resultant sheet product by calculating the wet weight minus dry weight divided by the sheet product's geometric wet volume.

Charge/Discharge cycling was performed on cells having the subject sheet using a Princeton Applied Research Model 363 galvanostat. The galvanostat was

powered and monitored with an Analog Devices MAC 5000 microcomputer which controlled the current passing through the cell and measured the current passing through the cell and measured the current voltage and charge throughout the cycle.

The following examples are given for illustrative purposes only and are not meant to be a limitation on the subject invention, except as made in the claims appended hereto. All parts and percentages are by weight unless otherwise indicated.

Example 1

Eight parts of high density polyethylene of a weight average molecular weight of 250,000 were mixed with 22 parts of hydrocarbon oil (Sunthene 255; density of 0.89g/ml, 54 ssu at 210°F, flash point of 390°F), 19 parts of Shawinigan processed carbon black (acetylene black, 50% compressed density of 2.1 gm/cc, 70 m<sup>2</sup>/gm BET surface area) 3 parts of graphitic carbon (density of 2.1 gm/cc, 5 m<sup>2</sup>/gm BET surface area) and 54 parts of minus 200 mesh V<sub>2</sub>O<sub>5</sub> (Cerac). The mixture was placed in a Brabender blender maintained at a temperature of 150°C and mixed for about 5 minutes until steady torque is obtained. A dry nitrogen atmosphere was maintained over the equipment.

A sample of the resultant composition was hot pressed at a pressure of about 250 psi at a temperature of 150°C for approximately 10 seconds to produce a uniform sheet of 18 mil thickness. The formed sheet was then immersed in cyclohexane for 3 periods of 10 minutes each to yield a microporous sheet having 36 percent void volume substantially uniformly distributed throughout. The composition of the extracted, microporous sheet was 9.5 percent polyethylene, 26.2 percent combined particulate

carbon, 64 percent  $V_2O_5$  and less than 1 percent oil. The electronic conductivity of the microporous sheet measured at  $22^\circ\text{C}$  and  $1\text{ KH}_2$  was  $0.11\text{ ohm}^{-1}\text{ cm}^{-1}$ .

#### Example 2

A cathodic electrode was formed with the composition of Example 1 above and the electrode was used as part of a  $\text{Li-V}_2\text{O}_5$  battery cell. Two sheets (approx. 3 mils each) were formed by pressing samples of the composition of Example 1 above at  $150^\circ\text{C}$  and 250 psi. The sheets were placed on each side of an expanded nickel metal screen and the composite subjected to pressure of 250 psi at  $150^\circ\text{C}$  for approximately 10 seconds to produce a product having the screen embedded therein. An examination of the product showed that the polymeric sheets had formed into a single unitary structure. The product was immersed in cyclohexane bath for 3 periods of 10 minutes each to yield a microporous polymer bonded electrode product. The electrode was then dried at 10 - 20 microns vacuum and  $80^\circ\text{C}$  for 2 hours to remove residual amounts of solvent. The formed cathodic electrode was placed in an Argon atmosphere glove box for assembly as part of a cell with a lithium foil of  $1\text{ cm}^2$  and 5 mil thickness which had been pressed onto a commercially available expanded nickel metal grid. The two electrodes were placed into a rectangular glass tubing using a commercial polypropylene microporous sheet separator between the electrodes. The cell was filled with 0.5 ml  $1.2\text{M LiAsF}_6$  in 2-methyltetrahydrofuran. The cell was then temporarily sealed with an O ring, taken out of the glove box and permanently glass sealed in a flame.

The cell contained 13.1 mg  $V_2O_5$  which is equivalent to a theoretical capacity of 4.1 mAh (assuming the

-40-

discharged material is  $\text{Li}_2\text{V}_2\text{O}_5$ ). The cell was discharged at 1 mA to a cutoff voltage of 1.80 volts and charged at 0.5 mA to a cutoff voltage of 3.0 volts. Capacity utilization at 1 mA was 100% for Cycle #1, 65% for Cycle #3, 37% for Cycle #14 and 36% for Cycle #30. Because of the high theoretical capacity of this  $\text{V}_2\text{O}_5$  electrode system, the charge density was still very high even at the relatively low capacity percentage obtained.

### Example 3

Eight parts of high density polyethylene of a weight average molecular weight of 250,000 were mixed with 22 parts of hydrocarbon oil (Sunthene 255; density of 0.89 g/ml, 54 ssu at 210°F, flash point of 390°F), 19 parts of Shawinigan processed carbon black (acetylene black, 50% compressed, 3 parts graphitic carbon and 65 parts of  $\text{FeS}_2$  (Cerac; minus 100 mesh, 99.9 percent purity). The mixture was processed in the same manner as described in Example 1 above. The composition of the formed sample of extracted microporous sheet product was: 8 percent polyethylene, 27 percent combined carbons and 65 percent  $\text{FeS}_2$ . The oil content was negligible. The electronic conductivity of the formed microporous sheet measured at 1 KHZ and 22°C was  $0.6 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

A Li- $\text{FeS}_2$  cell was fabricated by the same procedure as described in Example 2 above using the polymer  $\text{FeS}_2$  composition of this example. The cell contained 12.9 mg of  $\text{FeS}_2$  (active) material, a 5 mil Li foil and approximately 0.5 ml of an electrolyte solution composed of 1 M  $\text{LiClO}_4$  in propylene carbonate. The cell was tested by conventional charge-discharge cycling procedure discharged at 1 mA to a cutoff voltage of 1 volt and charged at 0.25 mA to a voltage limit of 2.5 volts. The

Neu eingereicht / Newly filed  
Nouvellement déposé  
-41-

cell delivered 7 mAh in Cycle #1, 5.3 mAh in Cycle #4, and 3.9 mAh in Cycle #6. The theoretical capacity based on 2 electrons per iron atom is 5.8 mAh.

#### Example 4

The procedure described in Example 3 above was repeated except that the amount of carbon black was reduced to 18 parts and the amount of  $\text{FeS}_2$  was increased to 80 parts. The formed extracted sheet was composed of 7 percent polyethylene, 19 percent combined particulate carbons, 73 percent  $\text{FeS}_2$  and less than 1 percent oil. The electronic conductivity of the sheet, measured at 1 KHz and  $22^\circ\text{C}$  was  $0.4 \text{ ohm}^{-1} \text{ cm}^{-1}$ . A  $\text{FeS}_2$  electrode was made according to the procedure of Example No. 2 and a Li- $\text{FeS}_2$  cell was fabricated as described in Example No. 3. This cell contained 15.3 mg of  $\text{FeS}_2$ . The cell was discharged at 1 mA, and charged at 0.5 mA to 2.5 volts. The cell delivered 3.8 mAh to 1.3 volts over 5 charge/discharge cycles.

#### Example 5

The procedure of Example 1 was repeated using a mixture of components composed of 9 parts of high-density polyethylene of weight average molecular weight of 250,000, 21 parts hydrocarbon oil (Sunthene 255) and 104 parts of CuS (Cerac; minus 200 mesh, 99.5 percent purity). The formed extracted microporous sheet was composed of about 8 percent polyethylene, 92 percent CuS and residual oil. Conductivity of the sheet, measure at 1 KHz and  $22^\circ\text{C}$  was  $3.3 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

A Li-CuS cell was fabricated using the material of this Example according to the procedure described in Example 2. The cell which contained 18.6 mg of CuS was

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Nouvellement déposé

discharged at 2 mA to 1.3 V and charged at 1 mA to 2.5 V. The maximum capacity obtained on discharge was 5.4 mAh which is equivalent to 1.03 Li ions per copper atom.

#### Example 6

Twelve parts of high density polyethylene of a weight average molecular weight of 250,000 were mixed with 18 parts of hydrocarbon oil (Sunthene 255; density of 0.89g/ml, 54 ssu at 210°F, flash point of 390°F), 23 parts of Shawinigan processed carbon black (acetylene black, 50% compressed density of 2.1 gm/cc, 70 m<sup>2</sup>/gm BET surface area), 4 parts of graphitic carbon (density of 2.1 gm/cc, 5 m<sup>2</sup>/gm BET surface area) and 46 parts of minus 200 mesh TiS<sub>2</sub> (average particle size of 15 microns). The mixture was placed in a Brabender blender maintained at a temperature of 150°C and mixed for about 5 minutes until steady torque is obtained. A dry nitrogen atmosphere was maintained over the equipment.

A sample of the resultant composition was hot pressed at a pressure of about 250 psi at a temperature of 150°C for approximately 10 seconds to produce a uniform sheet of 18 mil thickness. The formed sheet was then immersed in cyclohexane for 3 periods of 10 minutes each to yield a microporous sheet having 36 percent void volume substantially uniformly distributed throughout. The composition of the extracted, microporous sheet was 16 percent polyethylene, 22.6 percent combined particulate carbon, 61.3 percent TiS<sub>2</sub> and less than 1 percent oil. The electronic conductivity of the microporous sheet measured at 22°C and 1 KH<sub>2</sub> was 1.0 ohm<sup>-1</sup> cm<sup>-1</sup>.

Example 7

A cathodic electrode was formed with the composition of Example 1 above and the electrode was used as part of a Li-TiS<sub>2</sub> battery cell. Two sheets (approx. 1 mil) were formed by pressing samples of the composition of Example 1 above at 150°C and 250 psi. The sheets were placed on each side of an expanded nickel metal screen and the composite subjected to pressure of 250 psi at 150°C for approximately 10 seconds to produce a product having the screen embedded therein. An examination of the product showed that the polymeric sheets had formed into a single unitary structure. The product was immersed in cyclohexane bath for 3 periods of 10 minutes each to yield a microporous polymer bonded electrode product. The electrode was then dried at 10 - 20 microns vacuum and 80°C for 2 hours to assure removal of any residual amounts of solvent. The formed cathodic electrode was placed in an Argon atmosphere glove box for assembly as part of a cell with a lithium foil of 1 cm<sup>2</sup> and 15 mils thick which had been pressed onto a commercially available expanded nickel metal grid. The two electrodes were placed on each side of a commercial polyethylene microporous sheet separator and the assembly placed into a rectangular glass tubing. The cell was filled with 1.2M LiAsF<sub>6</sub> in 2-methyltetrahydrofuran. The cell was then temporarily sealed with an O ring, taken out of the glove box and permanently glass sealed in a flame.

The cell contained 4.2 mg TiS<sub>2</sub> which is equivalent to a theoretical capacity of 1 mAh. The cell was discharged at 2 - 4 mA to a cutoff voltage of 1.5 volts and charged at 1 - 1.8 mA to a cutoff voltage of 2.5 volts. Capacity utilization at 2 mA was 100% for Cycle #1, 78% for Cycle #70, 65% for Cycle #765 and 50% for Cycle #1225. Capacity

utilization at 4 mA discharge for cycle #120 was 71%. The above data demonstrates the unexpected superior capacity utilization of the electrode product of the present invention attainable over many cycles. The figure of merit for the subject  $TiS_2$  electrode (the actual number of times that each molecule of  $TiS_2$  has been discharged and charged) (also referred to as turnover number) was 820. When the present figure of merit number is compared to a very low figure of merit value of 8 which is reported in U.S. Patent 4,322,317 one is able to observe the distinct difference of the presently achieved product over that of the referenced product. The coulombic efficiency of the  $TiS_2$  electrode defined as charge in divided by charge out was  $100.0 \pm 0.3\%$  and the capacity fade rate averaged  $0.03\%$  per cycle, which is an exceedingly low value.

#### Example 8

Five parts of high density polyethylene of a weight average molecular weight of 3 million were mixed with 23 parts of hydrocarbon oil (Sunthene 255; density of 0.89 g/ml, 54 ssu at  $210^\circ F$ , flash point of  $390^\circ F$ ), 10 parts of Shawinigan processed carbon black (acetylene black, 50% compressed), 3 parts graphitic carbon and 62 parts of  $TiS_2$  (Cerac; minus 200 mesh, average particle size of 15 microns). The mixture was processed in the same manner as described in Example 1 above. The composition of the formed sample of extracted microporous sheet product was: 6 percent polyethylene, 16 percent combined carbons and 78 percent  $TiS_2$ . The oil content was negligible. The void volume was 45 percent and microporosity was uniform throughout. The electronic conductivity of the formed microporous sheet measured at 1 KHZ and  $22^\circ C$  was  $0.5 \text{ ohm}^{-1} \text{ cm}^{-1}$ .

A Li-TiS<sub>2</sub> cell was fabricated by the same procedure as described in Example 2 above using the polymer TiS<sub>2</sub> composition of this example. The cell was tested by conventional charge-discharge cycling procedure discharged at 2 mA to a cutoff voltage of 1.6 volt and charged at 1 mA to a voltage limit of 2.6 volts. The utilization (% of theoretical) of the TiS<sub>2</sub> electrode was 68% at Cycle #1, 60% at Cycle #40 and 40% at Cycle #61.

#### Example 9

The procedure of Example 1 was repeated using a mixture of components (same material as Example 1) composed of 8 parts of high-density polyethylene of weight average molecular weight of 250,000, 19 parts hydrocarbon oil, 13 parts carbon black, 4 parts graphitic carbon and 62 parts of TiS<sub>2</sub>. The formed extracted microporous sheet was composed of about 9.2 percent polyethylene, 19.5 percent combined carbon, 71.3 percent TiS<sub>2</sub> and neg. oil. Conductivity of the sheet, measure at 1 KHz and 22°C was 0.83 ohm<sup>-1</sup> cm<sup>-1</sup>.

A Li-TiS<sub>2</sub> cell was fabricated using the material of this Example according to the procedure described in Example 2. The TiS<sub>2</sub> electrode had a theoretical capacity of 2.83 mAh and the Li capacity was 27 mAh. The cell was discharged at 2 mA/cm<sup>2</sup> to 1.5 volts and charged at 1 mA at 2.6 volts. It delivered 83% of the theoretical TiS<sub>2</sub> capacity on Cycle No. 4, 70% of theoretical TiS<sub>2</sub> capacity on Cycle No. 108 and 50% of theoretical TiS<sub>2</sub> capacity on Cycle No. 230. The cell cycle life was limited by the Lithium electrode. The coulombic efficiency for the charge discharge cycles was 100.0±0.2%. This number represents the efficiency of the TiS<sub>2</sub> electrode as the Li was in excess.

Example 10

Nine parts of high density polyethylene of a weight average molecular weight of 250,000 were mixed with 21 parts of hydrocarbon oil (Sunthene 255; density of 0.89g/ml, 54 ssu at 210°F, flash point of 390°F), 14 parts of Shawinigan processed carbon black (acetylene black, 50% compressed density of 2.1 gm/cc, 70 m<sup>2</sup>/gm BET surface area), 1 part of graphitic carbon (density of 2.1 gm/cc, 5 m<sup>2</sup>/gm BET surface area) and 55 parts of minus 200 mesh TiS<sub>2</sub> (average particle size of 15 microns, battery grade). The mixture was placed in a Brabender blender maintained at a temperature of 150°C and mixed for about 5 minutes until steady torque is obtained. A dry nitrogen atmosphere was maintained over the equipment.

A sample of the resultant composition was hot pressed at a pressure of about 250 psi at a temperature of 150°C for approximately 10 seconds to produce a uniform sheet of 18 mil thickness. The formed sheet was then immersed in cyclohexane for 3 periods of 10 minutes each to yield a microporous sheet having 40 percent void volume substantially uniformly distributed throughout. The composition of the extracted, microporous sheet was 11 percent polyethylene, 19 percent combined particulate carbon, 70 percent TiS<sub>2</sub> and negligible amount of oil. The electronic conductivity of the microporous sheet measured at 22°C and 1 KH<sub>2</sub> was 0.42 ohm<sup>-1</sup> cm<sup>-1</sup>.

A Li-TiS<sub>2</sub> battery cell was built using the above material. 493 parts of the sheet product formed above was hot pressed onto a 20 cm<sup>2</sup> expanded nickel grid to produce a TiS<sub>2</sub> cathodic electrode product. A spirally wound cell was constructed in an Argone atmosphere glove box by placing the cathodic electrode adjacent one side of a commercial microporous separator sheet and an anodic

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electrode formed from 190 parts of Li foil pressed onto an expanded nickel grid adjacent the opposite side of the separator sheet. The assembly was jelly roll wound and placed into a cylindrical glass tube. The tube was filled with a solution of 1.2 M  $\text{LiAF}_6$  in 2-methyltetrahydrofuran and sealed to form the cell. The cell was discharged at 60 mA and charged at 30 mA between voltage limits of 1.6 and 2.6 volts. The capacity utilization of the 82.5 mAh  $\text{TiS}_2$  electrode was 87% at Cycle #10; 83% at Cycle #70; 80% at Cycle #100 and 50% at Cycle #165.

#### Example 11

(a) 8 parts of a high density polyethylene having a weight average molecular weight of 250,000 were mixed with 21 parts of hydrocarbon oil (Sunthene 255: density of 0.89 g/ml, 54 ssu at  $210^\circ\text{F}$ , flash point of  $390^\circ\text{F}$ ) and 84 parts of a commercially available battery grade titanium disulfide having an average particle size of 10 microns. The mixture was compounded in a Brabender maintained at  $150^\circ\text{C}$  for two 10 minute periods. The resultant homogeneous mixture was pressed into flat sheets using a flat plate press (Wabash) maintained at  $150^\circ\text{C}$  at a pressure of 400 psi to obtain sheets of 14.5 mils. thickness.

(b) An expanded Ni screen (5 mils. thick) having a nickel tab attached to one end was placed adjacent to a sheet formed in the manner described in paragraph (a) above. The composite was pressed using a flat plate press (Wabash) maintained at  $150^\circ\text{C}$  and 500 psi pressure. The pressed product was observed to be a unitary structure having the screen embedded within. The pressed sheet was then immersed in cyclohexane bath for 15 minutes and then

vacuum dried. The porosity of the sheet was about 40 percent. This sheet was then immersed in a 38 vol. percent solution of hydrocarbon oil (Sunthene 255) in cyclohexane to have a fixed amount of oil absorbed by the sheet. The sheet was removed from the solution and dried to permit the cyclohexane to evaporate. The electrode was pressed once more to remove the voids, then the oil was removed by extraction as described above and finally dried.

The resultant electrode was composed of 8.7 weight percent polyethylene and 91.3 weight percent titanium disulfide having a pore volume of 20 vol. percent.

#### Example 12

The electrode of Example I above was placed in an Argon atmosphere glove box and used to fabricate a spirally-wound Li-TiS<sub>2</sub> battery cell. The cell was formed from lithium foil, commercial microporous polypropylene separator, the electrode of Example I and 5 mil of electrolyte solution composed of 1.5 M LiAsF<sub>6</sub> in 2-methyl tetrahydrofuran.

The solid components of the cell will fit into a standard AA size cell with the electrolyte being in excess. The cell was sealed in glass tubing, evacuated and then filled with the electrolyte solution through a Ni tube which was subsequently sealed. The cell contained 1.14 Ah of TiS<sub>2</sub> and 1.80 Ah of Li.

The cell was discharged to 1.6 volts and charged to 2.6 volts. The cell delivered 0.96 Ah (84% of theoretical) (1 mA/cm<sup>2</sup>) at 190 mA in cycle No. 7 and 0.68 Ah (63% of theoretical) at the same rate at cycle No. 71.

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### Example 13

Sheets were formed in the same manner as described in Example I above except that 8 parts of polyethylene were mixed with 19 parts of hydrocarbon oil and 89 parts of  $\text{TiS}_2$ . Two sheets were positioned on each side of a nickel expanded screen and pressed into a unitary sheet and then subjected to two fresh baths of cyclohexane to extract substantially all of the oil. The electrode sheet was then immersed in a 38 vol. percent solution of hydrocarbon oil (Sunthene 255) in cyclohexane to allow sufficient oil pick-up to form the desired product void volume. The sheet was dried and pressed to remove excess voids as described in Example I above and then the oil contained in the sheet is removed by extraction with final drying.

A small rectangular glass sealed cell was built using the above electrode with lithium foil and an electrolyte solution composed of 1.2M  $\text{LiAsF}_6$  in 2-methyl tetrahydrofuran. The cell was discharged to 1.6 V and charged to 2.6 V. The utilization of the  $\text{TiS}_2$  electrode (% of theoretical) was 90 percent for cycle No. 3 ( $1 \text{ mA/cm}^2$ ); 81 percent for cycle No. 28 ( $1.5 \text{ mA/cm}^2$ ) and 75% for cycle No. 65 ( $1.5 \text{ mA/cm}^2$ ). The charge density of this electrode was  $0.9 \text{ mAh/cm}^2\text{-mil}$ . The fade rate was very low.

### Example 14

This example is made for comparative purposes.

A. A sheet product was formed in the same manner as described in Example III above except that only the initial extraction step was performed. The resultant electrode sheet was composed of 8.3 weight percent polyethylene and 91.7 weight percent  $\text{TiS}_2$  and had a void volume of 36 percent.

The electrode sheet was used as the cathode component of a rectangular cell fabricated in the same manner as described in Example III. The charge density of the  $\text{TiS}_2$  electrode was about  $0.7 \text{ mAh/cm}^2 \text{ mil}$ . The cell was discharged (at  $1 \text{ mA/cm}^2$ ) to 1.6 volts and charged to 2.6 volts. The cell delivered 92 percent of capacity at cycle No. 2 but only 60 percent of capacity at cycle No. 45. The observed large cell capacity fade was due to deterioration of the  $\text{TiS}_2$  cathode as the lithium and electrolyte were present in excess.

B. 4 parts of polyethylene having a weight average molecular weight of  $5 \times 10^6$  were mixed with 20 parts of hydrocarbon oil (Sunthene 255) and 105 parts of commercially available battery grade  $\text{TiS}_2$  having an average particle size of 10 microns. The mixture was processed into an electrode in the same manner as described in Example I above. The resultant electrode was used to form a  $\text{Li-TiS}_2$  rectangular cell as described in Example III above.

The cell was discharged at  $1 \text{ mA/cm}^2$  to 1.6 volts and charged at  $0.35 \text{ mA/cm}^2$  to 2.6 volts. The  $\text{TiS}_2$  capacity utilization was 95% for cycle No. 2; 71% at cycle No. 10; and 60% at cycle No. 18. The large capacity fade was due to  $\text{TiS}_2$  electrode deterioration as lithium and electrolyte were in excess.

#### Example 15

A first or active sheet was formed by mixing 8 parts of high density polyethylene of a weight average molecular weight of 250,000 with 19 parts of low aromatic petroleum hydrocarbon oil (Sunthene 255; density of  $0.89 \text{ g/ml}$ , 54 ssu at  $210^\circ\text{F}$ , flash point of  $390^\circ\text{F}$ ), 13 parts of Shawinigan processed carbon black (50%

compressed acetylene black, 45 millimicron, apparent density of 0.1 g/cc, 70 m<sup>2</sup>/g BET surface area) 4 parts graphitic carbon and 62 parts of a commercial battery grade TiS<sub>2</sub> (average particle size of 15 microns). The mixture was placed in a Brabender blender maintained at a temperature of 150°C and mixed for about 5 minutes until steady torque is obtained. A nitrogen atmosphere was maintained over the equipment.

A sample of the resultant composition was hot pressed at a pressure of about 250 psi at a temperature of 150°C for approximately 10 seconds to produce a uniform sheet of about 2 mils. thickness. The electronic conductivity of samples of the formed sheet, measured at 22°C and 1KHz, was 0.8 ohm<sup>-1</sup> cm<sup>-1</sup>.

Two samples of the sheet formed above (each 0.7 cm x 1.5 cm x 2.2 mil. thick) were placed on each side of an expanded nickel metal screen and the composite was pressed at 150°C and about 150 psi to form a sheet 5 mils. thick with only a single nickel wire welded to the screen left exposed.

A second or passive sheet was formed by mixing 15 parts high density polyethylene of a weight average molecular weight of 250,000, 49 parts of TiO<sub>2</sub> (BET surface area of 50 m<sup>2</sup>/g), 25 parts of a low aromatic petroleum hydrocarbon oil (Sunthene 255) and 0.1 part of commercial antioxidant (Santonox). The mixture was placed in a Brabender blender maintained at 150°C and mixed for about 6 minutes. A sample of the formed composition was pressed between two sheets of Mylar at 150°C and 250 psi to give a 2 mil. thick sheet. The electronic conductivity of this sheet was measured at 22°C and 1 KHz and determined to be negligible as it was not registerable at the lowest level of the bridge ( $4 \times 10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>).

Example 16

Two pieces of the passive sheet formed according to Example I B, above, were placed on each major surface of the active  $\text{TiS}_2$  sheet formed according to Example I A, above, in a manner to have the passive sheets extend beyond the edges of the active sheet by 2 millimeters on all edges. The composite was pressed at  $150^\circ\text{C}$  and about 25 - 50 psi for about 1 minute. The resultant sheet product was immersed in cyclohexane bath for 3 periods of 10 minutes each to yield a microporous sheet. The resultant electrode product was examined and had a fused unitary structure about 9.5 mils. thick with a surface composition of 23 percent polyethylene, 76 percent  $\text{TiO}_2$ , less than 1 percent oil and approximately 45 percent porosity. The two surfaces were separated by an inner core having a composition of 9.2 percent polyethylene, 19.5 percent combined carbon, 71 percent  $\text{TiS}_2$  and less than 1 percent oil with 36 percent porosity and having the nickel screen embedded therein.

Example 17

The electrode product of Example II was placed into an Argon atmosphere glove box for assembly as part of a cell with a lithium foil of  $1\text{ cm}^2$  and 2 mil. thickness supported on an expanded nickel screen which had a nickel wire extending therefrom. The electrode product and the lithium foil were positioned adjacent one another and placed into a rectangular glass container. The container was filled with a solution of 1.2 M  $\text{LiAsF}_6$  in 2-methyl tetrahydrofuran and sealed with an O ring seal, taken out of the Argon box and permanently heat sealed leaving the nickel wires exposed to produce a Li- $\text{TiS}_2$  cell. The cell

was discharged at 2 mA to a cutoff voltage of 1.5 volts and was charged at 1 mA to an upper voltage of 2.5 volts. The utilization of the 1.7 mAh ( $\text{TiS}_2$  limited) cell was 79% at Cycle No. 5, 73% at Cycle No. 100 and 50% at Cycle No. 160.

#### Example 18

A cathodic sheet product was formed by placing two 4 mil. sheets, formed from the same composition as described in Example 1 A above, on each side of an expanded nickel screen and then pressing the composite as described in Example I A (first sheet). A 2 mil. second sheet formed from the composition of Example I B was folded around the first sheet in a manner to leave 2 mm excess of the second sheet on all edges. Light pressure of about 25 psi was applied with a plate press at  $150^\circ\text{C}$  to effect fusing of the sheets and the edge portions to themselves. The sheet product was immersed in a cyclohexane bath for three 10 minute periods to extract the oil component. The resultant cathodic sheet product was put into an Argon atmosphere glove box. A  $\text{Li-TiS}_2$  cell was fabricated by spirally winding the formed cathodic sheet product directly with a 2 x 7 cm. 5 mil. lithium foil which is supported on an expanded nickel screen. The jelly roll electrodes were placed in a glass tube container which was then filled with 865 mg of an electrolyte solution composed of 1.2 M  $\text{LiAsF}_6$  in tetrahydrofuran. The container was sealed with an O ring seal, removed from the Argon box and permanently glass sealed.

This example represents the ease and ability of the subject cathodic sheet product to be readily manipulated and formed into a complex configuration and to form a cell without the utilization of additional components such as a

separator membrane or the like. The cell was cycled between 2.5 and 1.5 volts at a discharge current of 70 mA and a charging current of 30 mA. The utilization of the 100 mAh ( $\text{TiS}_2$  limited) cell was 72 percent after six cycles and 43 percent after 139 cycles.

#### Example 19

An inert portion of a cathodic electrode was formed from an initial composition comprising 12 parts of polyethylene ( $\text{MW}_w = 250,000$ ), 31 parts hydrocarbon oil (Sunthene 255), 23 parts silica (Hisil 233; BET surface area of  $110 \text{ m}^2/\text{g}$ ) and 0.1 part antioxidant (Santnox). A sheet (2 mil. thick) formed from this composition was folded around and fused to an active sheet of Example I A and then treated with cyclohexane, all in the manner described in Example IV above, to provide a unitary electrode product in which the active component is sealed in and forms the core of the product. A Li- $\text{TiS}_2$  cell was formed using the cathodic electrode product and 7 mg 5 mil. lithium foil in the manner described in Example III, above. The cell was cycled with a discharge to 1.5 volts at 2 mA and charged to 2.5 volts at 1 mA. The capacity utilization of the theoretical 2.9 mAh ( $\text{TiS}_2$  limited) was 76 percent after the sixth Cycle, 65 percent after the one hundredth Cycle and 50 percent at Cycle No. 200.

#### Example 20

A cathodic sheet product was formed by a core having a composition comprising a mixture of 5 parts of high density polyethylene having a weight average molecular weight of 3 million, 23 parts of hydrocarbon oil (Sunthene 255), 10 parts of Shawinigan processed carbon black (45 millimicron, apparent density of  $0.1 \text{ g/cc}$ ,  $70 \text{ m}^2/\text{g}$  BET

surface area), 3 parts graphitic carbon and 65 parts of a commercial battery grade  $\text{TiS}_2$  (average particle size of 15 microns). This composition was formed into a sheet at  $165^\circ\text{C}$  and 250 psi. The sheet was then encompassed in a passive composition of Example I B and readily fused into a unitary structure which was treated with cyclohexane in the manner described in Example II. The core of the product was 6 percent polyethylene, 16 percent combined carbon, and 78 percent  $\text{TiS}_2$  and had about 45 percent porosity. The surfaces of the product was 23 percent polyethylene, 76 percent  $\text{TiO}_2$  and less than 1 percent oil with about 45 percent porosity.

The above electrode product was used to form a  $\text{Li-TiS}_2$  cell in the same manner as described in Example III, above. The cell was cycled between 2.6 and 1.6 volts at a discharge/charge current of 2 mA/1 mA respectively. The utilization of the 3 mAh ( $\text{TiS}_2$  limited) cell was 61 percent after Cycle 5 and 54 percent after Cycle 35.

#### Example 21

The procedure of Example I A was repeated except that the  $\text{TiS}_2$  was replaced with 55 parts of vanadium oxide ( $\text{V}_2\text{O}_5$ , 200 mesh, 99.9 percent pure). The resultant sheet had a conductivity of  $0.4 \text{ ohms}^{-1} \text{ cm}^{-1}$ . An 8 mil. thick  $\text{V}_2\text{O}_5$  active sheet was formed having a nickel screen embedded therein.

A cathodic electrode was formed according to the procedure of Example V using the above  $\text{V}_2\text{O}_5$  active sheet and the sheet material of Example I B and was treated with cyclohexane as described in Example II.

The cathodic electrode described above was placed against a 5 mil. lithium foil and formed into a  $\text{Li-V}_2\text{O}_5$  cell by the procedure described in Example III, disclosed

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Nouvellement déposé

above. The cell has a theoretical  $V_2O_5$  limited capacity of 5.5 mAh (based on the reaction  $2Li + V_2O_5 \rightarrow Li_2V_2O_5$ ). The cell was discharged to 2V at 1 mA and charged at 0.5 mA to 3V. Capacity utilization (% of theoretical) was 100 at Cycle No. 1, 82 at Cycle No. 3, 49 at Cycle No. 5 and 40 at Cycle No. 25.

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## WE CLAIM:

1. A cathodic electrode suitable for use in a non-aqueous battery system comprising at least one substantially homogeneous, microporous sheet product having a composition of from about 70 - 98 weight percent of particulate material selected from electrochemically active particulate material and electrically conductive particulate material and mixtures thereof (preferably  $TiS_2$ ) alone or together with other metals, from about 2 - 30 weight percent of polyethylene having a weight average molecular weight of from about 150,000 to 5,000,000 (preferably from 200,000 to 500,000) and from 0 to about 5 weight percent of an organic plasticizer for said polyethylene; and a current collector composed of a conductive material, said collector being in intimate contact with each of said at least one microporous sheet product.

2. The electrode of Claim 1 wherein up to about 30 weight percent of said particulate material is composed of a conductive carbon black having an average particle size of from about 1 to 100 millimicrons and the remainder of said particulate material is selected from at least one metal chalcogenide having a metal selected from titanium, zirconium, hafnium, niobium, manganese, copper, iron, tantalum, chromium, vanadium or mixtures thereof (preferably the sole or major chalcogenide being  $TiS_2$  - having an average particulate size of 30 microns or less).

3. A microporous sheet product suitable for use in forming a cathodic polymer bonded electrode comprising

(a) from 70 - 98 weight percent of particulate material selected from electrochemically active and electrically conductive material and mixtures thereof (preferably  $TiS_2$ ) alone or together with other metals; and

(b) from about 2 - 30 weight percent of polyethylene having a weight average molecular weight of from about 150,000 to about 5,000,000 (preferably 200,000 to 500,000); and

(c) from 0 to 5 weight percent of an organic plasticizer for said polyethylene;

said sheet having a void volume of at least about 10 volume percent and capable of exhibiting conductivity of at least about 0.1 reciprocal ohm-cm. when placed in an electrical circuit.

4. A cathodic electrode suitable for use in a non-aqueous battery system comprising at least one substantially homogeneous, microporous sheet product (preferably having a total thickness of less than 50 mils) having a void volume of from 15 to 25 volume percent and having a composition of from about 90 - 94 weight percent of particulate material consisting essentially of titanium disulfide having an average particle size of less than about 30 microns, from about 6 - 10 weight percent of polyethylene having a weight average molecular weight of from about 200,000 to 500,000 and from 0 to about 2 weight percent of an organic plasticizer for said polyethylene; and a current collector composed of a conductive material, said collector being in intimate contact with each of said at least one microporous sheet product.

5. A microporous sheet product suitable for use in forming a cathodic polymer bonded electrode comprising:

a) from about 90 to 94 weight percent titanium disulfide having an average particle size of less than about 30 microns;

b) from about 6 to 10 weight percent of polyethylene having a weight average molecular weight of from about 200,000 to 500,000; and

c) from 0 to about 2 weight percent of an organic plasticizer for said polyethylene; said sheet being substantially homogeneous, microporous and having a void volume of from 15 to 25 percent and capable of exhibiting conductivity of at least 0.15 reciprocal ohm-cm.

6. An electrode product comprising a substantially unitary, microporous structure having a first and a second major surface and a thickness of less than about 50 mils, each of said first and second major surface and a thickness adjacent to each major surface composed of a substantially homogeneous outer composition of from about 7 to 35 weight percent of a polyolefin having a weight average molecular weight of at least about 100,000, from about 50 to 93 weight percent of an inert filler having a mean particle size of from about 0.01 to 10 microns and from 0 to about 15 weight percent of an organic plasticizer for said polyolefin, each of the first and second major surface outer composition being separated by a thickness composed of a substantially homogeneous core composition of from about 2 - 30 weight percent polyethylene of a weight average molecular weight of at least about 150,000, from 70 - 98 weight percent of particulate material selected from electrically conductive particulate material, electrochemically active particulate material and mixtures thereof and from 0 to about 5 weight percent of an organic plasticizer for said polyethylene and a current collector of electronically conductive material in contact with said particulate material.

7. The electrode product of Claim 6 wherein the particulate material has a mean particle size of about 25 microns or less and is composed of from about 70 to 100 weight percent of at least one metal chalcogenide of a metal selected from titanium, zirconium, hafnium, niobium, tantalum, vanadium and mixtures thereof (preferably  $TiS_2$ ) and from 0 to about 30 weight percent of a conductive carbon black.

8. The electrode product of Claim 6 wherein the polyethylene is present in 2 - 15 weight percent and has a weight average molecular weight of from about 200,000 to 500,000, the particulate material is present in 85 - 98 weight percent and is at least about 70 (preferably 100) weight percent titanium disulfide, the plasticizer for the polyethylene is present in from 0 - 5 weight percent and is selected from a petroleum oil, the polyolefin is present in from 7 - 50 weight percent and has a weight average molecular weight of from 150,000 to 500,000, the inert filler is selected from titania, alumina, silica and the polyolefin plasticizer is a petroleum oil.

9. A process for forming a microporous sheet product suitable for use as a cathodic electrode comprising;

(a) forming a substantially uniform mixture comprising from about 3 to 30 volume percent of polyethylene having a weight average molecular weight of from about 200,000 to about 500,000, from about 27 to about 76 volume percent of particulate titanium disulfide having an average particle size of less than about 20 microns, and from about 20 to 70 volume percent of plasticizer for the polyethylene;

(b) shaping the substantially uniform mixture into an initial sheet;

(c) forming from the initial sheet an intermediate sheet having from 10 to 22 volume percent plasticizer;

(d) compressing the intermediate sheet to provide a substantially nonporous compressed intermediate sheet; and

(e) removing substantially all of the plasticizer from said compressed intermediate.

10. In a primary or secondary battery comprising at least one pair of electrodes of opposite polarity, and an electrolyte and wherein said anodic electrode is composed of an alkali metal or alloy thereof, the improvement comprises that said cathodic electrode consists essentially of the electrode product of Claim 9.

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## UEXKÖLL &amp; STOLBERG

PATENTANWÄLTE

BESELERSTRASSE 4

D-2000 HAMBURG 52

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Application No.: 87104027.5  
 Applicant: W. R. Grace & Co.

This is in response to the Office Action dated July 2,  
 1987.

Attached is a detailed list of the corrections filed  
 on April 28, 1987.

It is respectfully requested to publish the corrections  
 together with the publication of the documents as origin-  
 ally filed.

For the Applicant:

Ingeborg Voelker

Encl.

For the purpose of publication <i>only</i>	
correction(s)	
<input checked="" type="checkbox"/>	allowed
<input type="checkbox"/>	allowed with exception of the deleted points
<input type="checkbox"/>	not allowed
Signature: <i>[Signature]</i>	date: 3/5/87
Receiving Section	

## List of Amendments

Page	Line	Original text	Amended text
43	3	Example 1	Example 6
44	25	Example 1	Example 6
45	12	Example 1	Example 6
45	13	Example 1	Example 6
48	15	Example I	Example II
49	3	Example I	Example II
49	29	Example III	Example 13
50	3	Example III	Example 13
50	17	Example I	Example II
50	19	Example III	Example 13
50	28		A.
51	21	-	B.
52	3	Example I B	Example 15 B
52	4	Example I A	Example 15 A
52	22	Example II	Example 16
53	10	Example I A	Example 15 A
53	12	Example I A	Example 15 A
53	13	Example I B	Example 15 B
54	14	Example I A	Example 15 A
54	16	Example IV	Example 18
54	20	Example III	Example 17
55	5	Example I B	Example 15 B
55	7	Example II	Example 16
55	15	Example III	Example 17
55	21	Example I A	Example 15 A
55	29	Example I B	Example 15 B
55	30	Example II	Example 16
55	33	Example III	Example 17

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correction(s)

☐ allowed☐ allowed with exception  
of the deleted points☐ not allowed

Signature:

date: 3/5/87

Receiving Section